

1) Please replace the paragraph beginning at page 6, line 17, with the following rewritten paragraph:

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The PASC coating 24 must be sufficiently thick so as to provide an acceptable level of PASC activity. There is no absolute value which renders the PASC coating 24 "acceptable" or "unacceptable" because whether a PASC coating has an acceptable level of PASC activity is largely determined by the purpose and conditions under which the PASC coated article is being used and the performance standards selected in connection with that purpose. In general, thicker PASC coatings provide higher PASC activity. However, other considerations may weigh toward a thinner coating, e.g. thinner coatings are preferred when the article is to have high transmission for aesthetic or optical reasons; the surface contaminants on the surface of the article are easily removed with a thinner PASC coating, the coating is exposed to substantial irradiation and/or the PASC coating 24 will be exposed to sodium ion poisoning discussed in more detail below. In a CVD process, a photocatalytically-active self-cleaning coating 24 is formed which may range from about 100Å to 2500Å thick. For a wide variety of applications, it is preferred that the PASC coating is at least about 200 Angstroms (Å), preferably at least about 400Å and more preferably at least about 500Å thick. It has been found that when the substrate 22 is a piece of float glass and the PASC coating 24 is an anatase titanium dioxide PASC coating formed directly over the piece of float glass by the CVD method, that a thickness of at least about 500Å provides a PASC reaction rate in the range of about  $2 \times 10^{-3}$  to about  $5 \times 10^{-3}$  per centimeter minute (hereinafter "cm<sup>-1</sup>min<sup>-1</sup>") for the removal of a stearic acid test film when the PASC coating was exposed to ultraviolet radiation from a light source such as that sold under the tradename UVA-340 by the Q-Panel Company of Cleveland, Ohio, having an intensity of about 20 watts per square meter (hereinafter W/m<sup>2</sup>) at the PASC coating surface which is acceptable for a wide range of applications.

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2) Also please replace the paragraph beginning at page 49, line 6, with the following paragraph:

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The results of the photocatalytic analysis shown in Table 6 suggest that a titanium dioxide layer thickness of about 625Å with no barrier layer (Sample I) can approach the PASC activity of a thinner 400Å PASC coating over an SIDB layer (Sample J). It should be noted that for Samples J, the SIDB layer underwent an intermediate cooling and subsequent reheating operation described, which reheating operation may have reduced the SIDB layer effectiveness for Sample J, which might otherwise have had a higher PASC activity.

3) Please replace the paragraph beginning at page 46, line 29, with the following paragraph:

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Referring now to Fig. 2, in an alternative method of preventing sodium ion poisoning of the PASC coating, an SIDB layer 26 is provided between the PASC coating 24 and the substrate 22. The SIDB layer 26 may be the only layer between the PASC coating 24 and the substrate 22, or it may be one layer of a multilayer stack. Where a multilayer stack is employed, it is not required that the SIDB layer 26 be in contact with the substrate 22, provided the SIDB layer 26 is positioned between the PASC coating 24 and the substrate 22 to prevent sodium ion numeral 27 as depicted in Fig. 2 migration from the substrate 22 to the PASC coating 24.

4) Please replace the paragraph beginning at page 30, line 15, with the following paragraph:

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The decreased PASC activity of Example 2 is believed to arise from the difference in titanium dioxide coating thickness between Examples 1 and 2, (about 2100Å versus about 700-800Å, respectively). More particularly, it is believed that the PASC reaction rate of Example 2 was lower than that

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of Example 1 due to the increased depth of sodium ion diffusion into the titanium dioxide coating of Example 2 as a larger percentage of the total thickness of the titanium dioxide PASC coating for the titanium dioxide PASC coating of Example 2 than that of Example 1. It is believed that sodium ions migrated from the glass sample into the PASC coating of Example 2 in annealing zone 98. One conclusion that may be drawn from a comparison of Examples 1 and 2 is that in the absence of an SDB layer, thicker PASC coatings are less susceptible to sodium ion poisoning, thus maintaining higher PASC activity.

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5) Also, if not already present in the captioned patent application, please replace the paragraph beginning at page 14 line 9 with the following rewritten paragraph which includes added sentences and also adds the following additional paragraphs:

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B<sup>6</sup>  
The preferred method to provide a PASC coating using the MSVD method is to sputter a coating on the substrate, remove the coated substrate from the MSVD coater and thereafter heat treat the coated substrate to crystallize the sputter coating into the PASC coating 24. For example, but not limiting to the invention, with the MSVD method, a target of titanium metal sputtered in an argon/oxygen atmosphere having about 5-50%, preferably about 20% oxygen, at a pressure of about 5-10 millitorr to sputter deposit a titanium dioxide coating of desired thickness on the substrate 22. The coating as deposited is not crystallized. The coated substrate is removed from the coater and heated to a temperature in the range of about 400°C (752°F) to about 600°C (1112°F) for a time period sufficient to promote formation of the PASC crystalline form of titanium dioxide to render PASC activity. Generally at least an hour at temperature in the range of about 400°C (752°F) to about 600°C (1112°F) is preferred. Where the substrate 22 is a glass sheet cut from a glass float ribbon,

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the PASC coating 24 may be sputter deposited on the air side and/or the tin side.

The substrate 22 having the PASC coating 24 deposited by the CVD, spray pyrolysis or MSVD methods may be subsequently subjected to one or more post-PASC coating annealing operations to increase the self-cleaning activity of the PASC coating 24. It is believed that such post-PASC coating annealing may increase self-cleaning activity of the PASC coating 24 by promoting formation of the desired PASC crystalline phase. As may be appreciated, the time and temperatures of the anneal may be affected by several factors, including the makeup of substrate 22, the makeup of PASC coating 24, the thickness of the PASC coating 24, and whether the PASC coating 24 is directly on the substrate 22 or is one layer of a multilayer stack on substrate 22. It has been determined that where the substrate 22 is a piece of float glass and the PASC coating is a 400Å or 625Å thick anatase titanium dioxide formed by the spray pyrolysis method, that annealing the coating at 500°C (932°F) for up to 13 minutes increased PASC activity.

As discussed above, whether the PASC coating is provided by the CVD process, the spray pyrolysis process or the MSVD process, where the substrate 22 includes sodium ions that can migrate from substrate 22 into the PASC coating deposited on substrate 22, the sodium ions may inhibit or destroy the photocatalytic activity of the PASC coating by -

6) Also if not already present in the captioned patent application, please replace the section of the paragraph beginning at page 15 line 15 with the following full paragraph:

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--As discussed above, whether the PASC coating is provided by the CVD process, the spray pyrolysis process or the MSVD process, where the substrate 22 includes sodium ions that can migrate from substrate 22 into the PASC coating deposited on substrate 22, the sodium ions may inhibit or

B<sup>7</sup> destroy the photocatalytic activity of the PASC coating by forming inactive compounds while consuming titanium e.g. by forming sodium titanates or by causing recombination of photoexcited charges.--

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7) Also if not already present in the captioned patent application, please replace the paragraph beginning on page 15 line 24 with the following rewritten paragraph which includes additional sentences and which is followed by additional paragraphs:

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B<sup>8</sup> --It has been found that when the thickness of the PASC coating exceeds a minimum threshold value, the PASC activity is not destroyed by sodium ion migration even though the PASC coating is deposited over the surface of a sodium-ion containing substrate while the substrate is at a temperature sufficient to cause migration of sodium ions from substrate into the PASC coating. While the mechanism for this result is not completely understood, it is believed that when the thickness of the PASC coating exceeds this minimum thickness, the sodium ions are able to migrate only through a fraction of the overall thickness of the PASC coating during the time period at which the temperature of substrate exceeds the temperature which permits sodium ion migration. Thereafter, when the temperature of substrate falls below that which causes sodium ion migration, the sodium ions migration stops or "freezes" in place, resulting in a thickness of the PASC coating opposite from the substrate surface free of sodium ion poisoning and able to maintain PASC activity. This minimum thickness of the PASC coating as may be appreciated by those skilled in the art varies with expected parameters such as, but not limited to, the time at which substrate is held above the temperature at which sodium ion migration occurs, the use to which the PASC article of manufacture is to be put and the degree of PASC activity desired or required. It has been found that for a CVD deposited titanium dioxide PASC coating over a piece of soda-lime-silica flat glass, the thickness of

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the PASC coating should be a minimum of about 250Å, preferably a minimum of about 400Å and more preferably a minimum of about 500Å to permit a sufficient portion of the PASC coating 24 to remain free of sodium ion poisoning and retain its PASC activity.

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Referring now to Fig. 2, in an alternative method of preventing sodium ion poisoning of the PASC coating, an SIDB layer 26 is provided between the PASC coating 24 and the substrate 22. The SIDB layer 26 may be the only layer between the PASC coating 24 and the substrate 22, or it may be one layer of a multilayer stack. Where a multilayer stack is employed, it is not required that the SIDB layer 26 be in contact with the substrate 22, provided the SIDB layer 26 is positioned between the PASC coating 24 and the substrate 22 to prevent sodium ion migration from the substrate 22 to the PASC coating 24.-

8) Also if not already present in the captioned patent application, please ~~replace~~ the section of the paragraph that begins on page 47 line 9 and ends on page 18 line 5 with the following complete paragraph:

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--The SIDB layer 26 may be formed of amorphous or crystalline metal oxides including but not limited to cobalt oxides, chromium oxides and iron oxides, tin oxides, silicon oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, and mixtures thereof. Mixtures include but are not limited to magnesium/aluminum oxides and zinc/tin oxides. As can be appreciated by those skilled in the art, the metal oxide may include oxides, super-oxides or sub-oxides of the metal. While the thickness of the SIDB layer necessary to prevent sodium ion poisoning of the PASC coating varies with several factors including the time period at which a substrate will be maintained at temperatures above which sodium ion migration occurs, the rate of sodium ion migration from the substrate, the rate of sodium ion migration through the SIDB layer, the

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thickness of the PASC coating and the degree of photocatalytic activity required for a given application, typically for most applications, the SIDB layer thickness should be in the range of at least about 100Å, preferably at least about 250Å and more preferably at least about 500Å thick to prevent sodium ion poisoning of the PASC coating layer. The SIDB layer may be deposited over substrate 22 by CVD, spray pyrolysis, or MSVD methods. Where the spray pyrolysis or CVD methods are employed, the substrate 22 is preferably maintained at a temperature of at least about 400°C (752°F) to ensure decomposition of the metal-containing precursor to form the SIDB layer. The SIDB layer may be formed by other methods, including the sol-gel method, which sol-gel method as noted above is not compatible with the manufacture of a glass float ribbon.-

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9) At page 14 after line 9 of the captioned patent application after the word "method", please insert the following paragraphs from U.S. Patent 4,379,040 column 7 line 42 through column 8 line 44 which was incorporated by reference in the specification at page 13 line 17:

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--It was customary to attain a desired degree of oxidation in titanium oxide films by an evaporation technique carried out in two distinct stages; first, by depositing titanium oxide in an under-oxidized state and thereafter, by introducing an oxidizing atmosphere thereto to attain the desired degree of oxidation. It has been found according to the present invention that the titanium oxide can be successfully magnetically enhanced sputtered onto the substrate with the degree of oxidation desired, thus eliminating the need for further oxidation. Deposition of ideally oxidized titanium oxide films is also more easily controlled in the practice of the present invention than heretofore, yielding a more consistent final product. It is believed that the preferred titanium oxide films deposited according to the present invention comprise a combination of

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titanium dioxide intermixed with atoms and/or small agglomerations of titanium metal, i.e. films of titanium oxide having greater than 1.7 but less than 2.0 parts oxygen to parts titanium, and preferably between 1.9 and 2.0. Such films may be characterized as having an optical extinction coefficient between about 0.03 and 0.3, preferably between 0.03 and 0.09, and most preferably between 0.06 and 0.08. The titanium oxide layer is preferably deposited with a thickness within the range of about 200 to 500 Angstroms to obtain the desired optical properties and film continuity.

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The titanium oxide layer can be deposited according to the present invention by magnetically sputtering a titanium metal cathode in an evacuated atmosphere having partial pressures of oxygen and argon. Initially, the coating chamber 12 is evacuated to less than  $3 \times 10^{-5}$  torr, after which an atmosphere of about 75% argon and 25% oxygen at a total pressure of about  $6 \times 10^{-4}$  torr is established. The cathode is activated at a preselected constant electrical power, and the deposition rate and total chamber pressure are established at preselected values. Upon reaching the desired coating conditions, the cathode is scanned across the surface of the substrate at a preselected rate to deposit a thin layer of an ideally oxidized film thereon. The luminous transmittance of the substrate is monitored during deposition by the photometer and photoelectric cell and decreases as the thickness of the film increases, from an initial value of about 90% for a glass substrate. Deposition rate, and therefore the degree of oxidation of the deposited titanium oxide film, is maintained constant either cyclically, or continuously, utilizing the embodiment of the invention. Deposition of the titanium oxide layer can be terminated when the luminous transmittance decreases to a value between about 72% and 76%, (about 80% to 85% of the transmittance of the uncoated substrate) a condition which is usually reached with a film thickness between about 300 Å and 350 Å, entailing about 5 to 7 passes of the cathode over the substrate. Generally during the above-described procedure, the oxygen input rate is gradually

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